Self-Assembling Rechargeable Li Batteries from Alkali and Alkaline-Earth Halides

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Project ID # bat326

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Overview

Timeline

- Project start: 10/01/2017
- Project end: 12/31/2019
- Percent complete: 75%

Budget

- Total project funding
  - DOE share: $1,250,000
  - Contractor share: $138,889
- Funding for 2018: $462,912
- Funding for 2019: $469,236

Barriers

- A. Cost
  - Higher energy cells as a way to reduce costs
- C. Life.
  - Beyond Li-ion (BLI, cells containing Li metal anodes) technologies suffer major cycle and calendar life issues.
- B. Performance
  - Need improvement in XFC (eXtreme Fast Charging)

Partners

- 24M Technologies Inc.

Relevance

Overall Objective

Investigate electrochemical formation of *self-assembling, self-healing solid electrolyte interfaces* on lithium metal anodes

Current Objective

- Structural and chemical characterization results for self-healed halide films on Li metal
- Establish quantitative criteria for effectiveness and reproducibility in dendrite-suppression experiments
- Demonstrate Li-Li symmetric cells that meet established criteria cycling at ≥ 3 mAh/cm^2 at C/5 rate >50 cycles

Impact

- A self-forming process is ***simple and scalable***.
- Enables very high energy density (>350 Wh/kg) rechargeable lithium batteries that could improve the driving range and reduce the cost for electric vehicles.

Milestones

Date	Description	Quarter	Status
June 2018	Deliver structural and chemical characterization results for self-healed halide films on Li metal	Q7	Completed
Sept. 2018	Establish quantitative criteria for effectiveness and reproducibility in dendrite-suppression experiments	Q8	Completed
Dec. 2018 Go/No-Go 2018	**Demonstrate Li-Li symmetric cells that meet established criteria cycling at ≥ 3 mAh/cm^2 at C/5 rate over 30 cycles**	**Q9**	**Completed**
March 2019	Demonstrate at least one Li-Li symmetric cell that cycles ≥3 mAh/cm^2 at C/5 rate over 50 cycles without short-circuit.	Q10	Completed
June 2019	Deliver 12 baseline cells of >10 mAh capacity for DOE testing Q11	Q11	On-track
Sept. 2019	Establish quantitative criteria for solid-electrolyte/liquid electrolyte combinations that exhibit self-healing functionality	Q12	On track

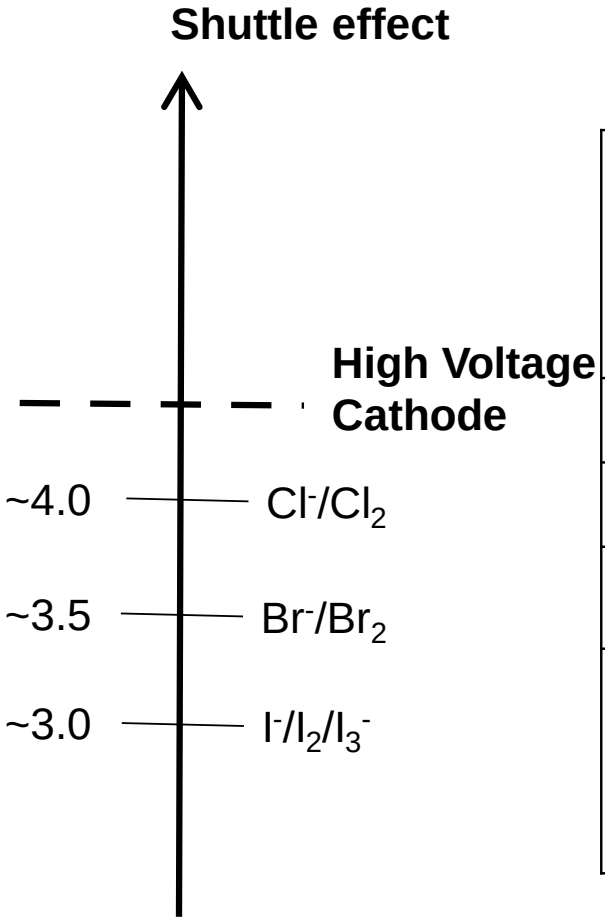
Approach

Starting paradigm: Spontaneous reaction between Li and I_2 self-forms a solid electrolyte/separator

Technical Approach

- **Descriptors:** Using structurally similar fluorinated organic compounds as model systems, we identify descriptors for high performing self-formed solid-electrolytes at lithium metal interface.
- **CE Measurement:** Using a newly developed technique for precise measurements of coulombic efficiency, we show clear correlation between our identified descriptors and high coulombic efficiency.
- **Full cell performance:** We integrate this understanding into a high-performing electrolyte formulation used in $LiCoO_2$-Li full cells with 50 μm lithium metal, that cycles for about 250 cycles to 80% capacity, delivering > 350 Wh/kg.

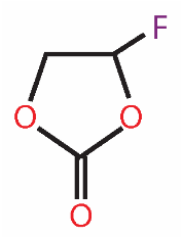
TECHNICAL ACCOMPLISHMENTS
Choice of Halide Component



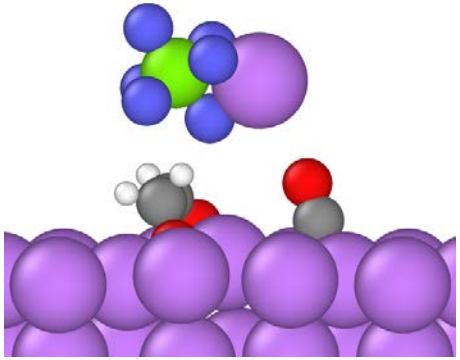
Insoluble

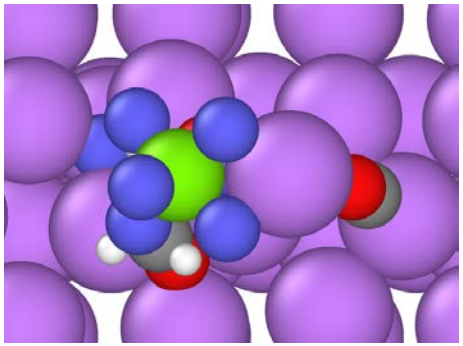
	1M $LiPF_6$ EC+DMC	**DMC**	**EC/DMC**
LiI	~ 3 M	1 M	1 M
LiBr	~ 1.5 M	< 1 M	< 1 M
LiCl	0.05 M	0.05 M	0.05 M
LiF	**Below detection**	**Below detection**	**Below detection**

TECHNICAL ACCOMPLISHMENTS
Fluorine-containing solvents as SEI formers

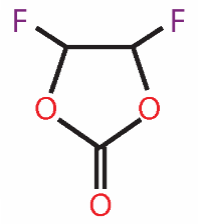


FEC

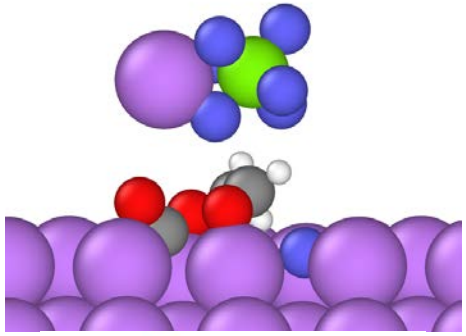


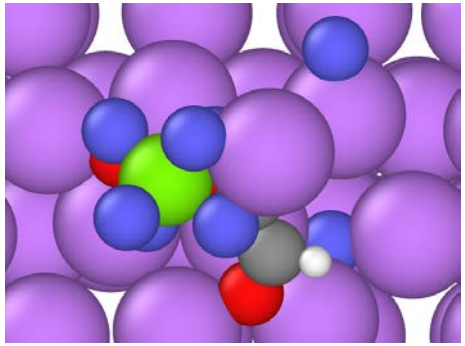


Complete ring breaking



DFEC





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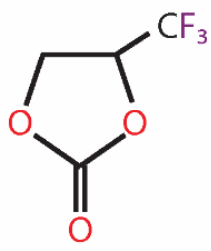
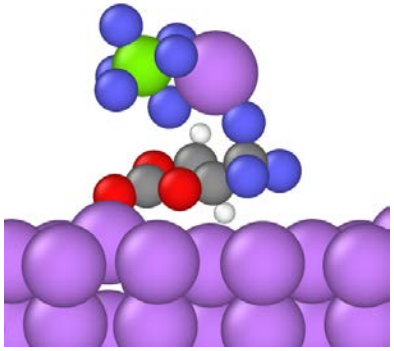
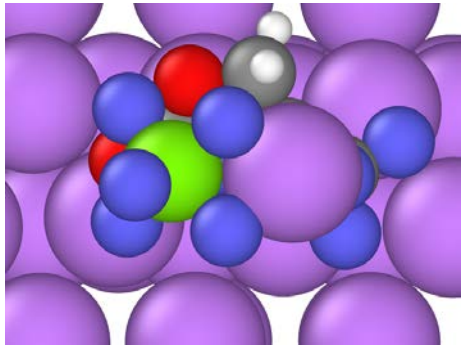


CF_3-EC

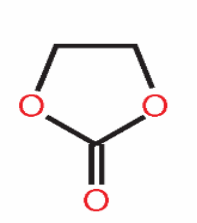




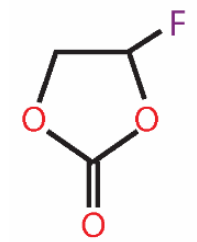
Completely intact!

TECHNICAL ACCOMPLISHMENTS

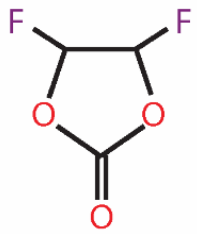
XPS Analysis for fluorine containing solvents



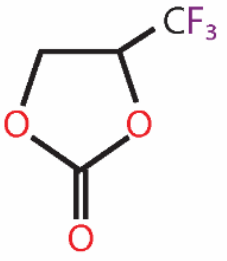
1.5 at.%



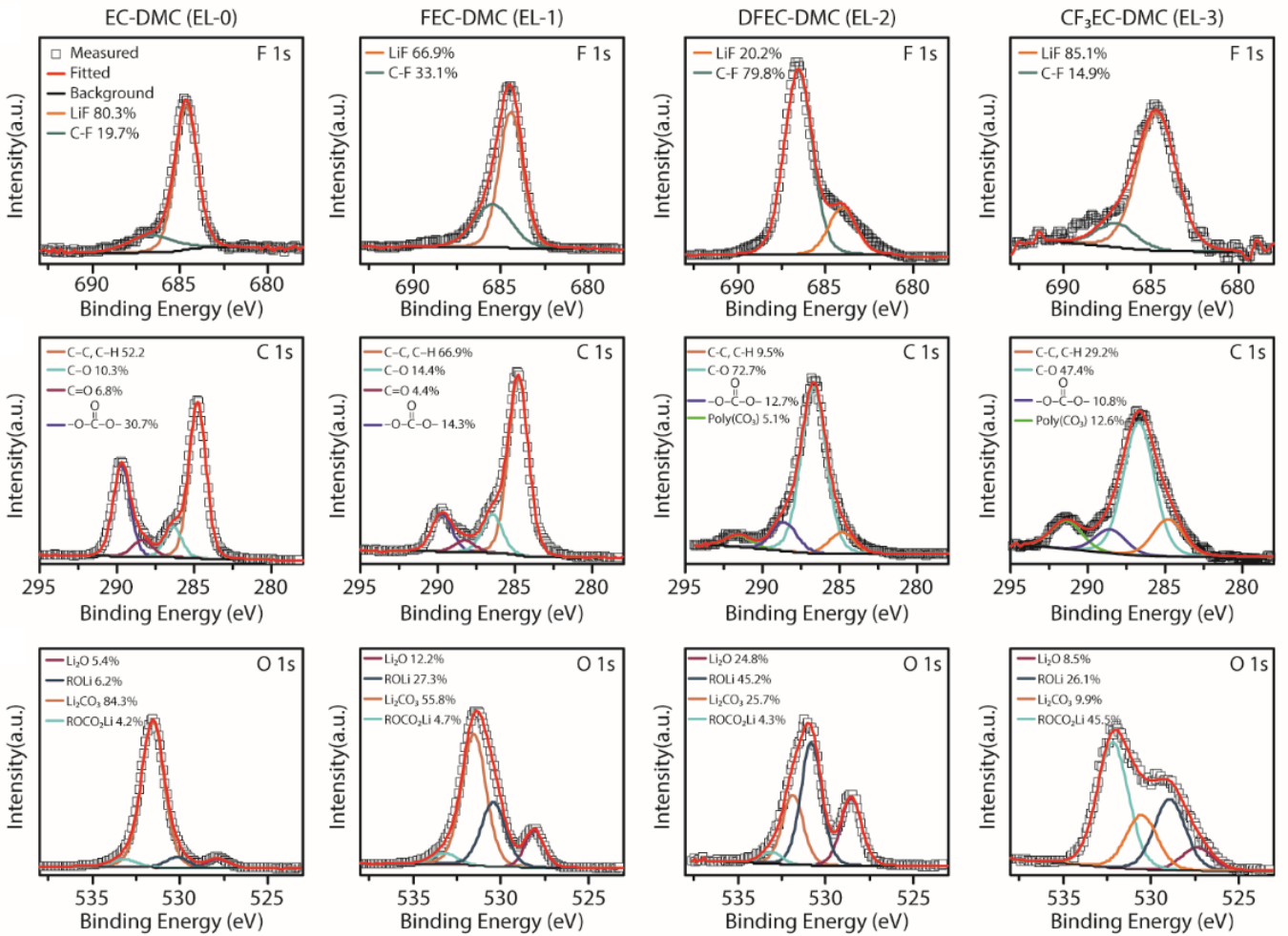
5.8 at.%



10.6 at.%



1.7 at.%

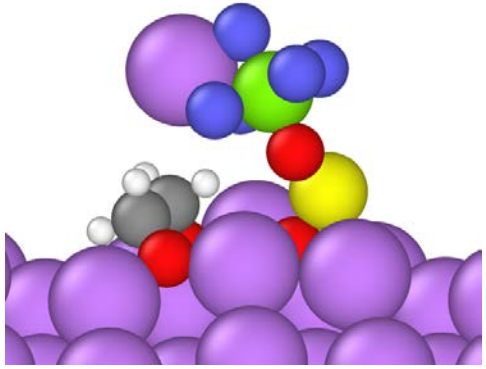


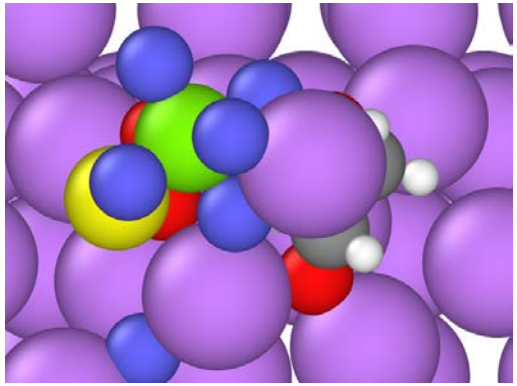
TECHNICAL ACCOMPLISHMENTS

Descriptors for Performance: Ionicity

Electrons transferred to the molecule during decomposition

Solvents	e^- transferred
DMC	2.0
EC	2.5
FEC	3.3
DFEC	4.4
CF_3EC	0.5
DTD	4.1



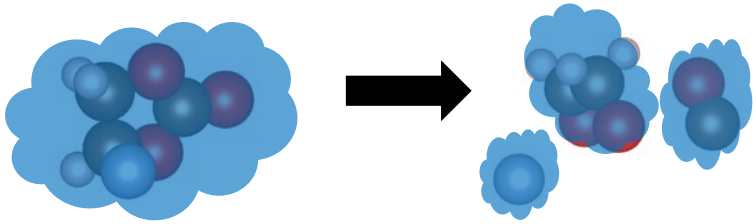


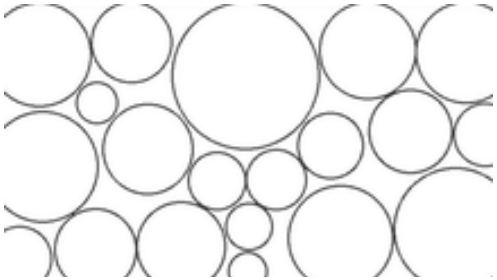
- Ionicity ∝ Bandgap
- Ionicity ∝ Mechanical Strength

Y. Zhu, V. Pande, L. Li,S. Pan, B. Wen, D. Wang, V. Viswanathan, Y.-M. Chiang, under review, arXiv:1903.09593.

TECHNICAL ACCOMPLISHMENTS
Descriptors for Performance: Compactness

Solvents	Volume of Largest SEI specie (Å³)
DMC	145
EC	132
FEC	89
DFEC	125
CF_3EC	169
DTD	97





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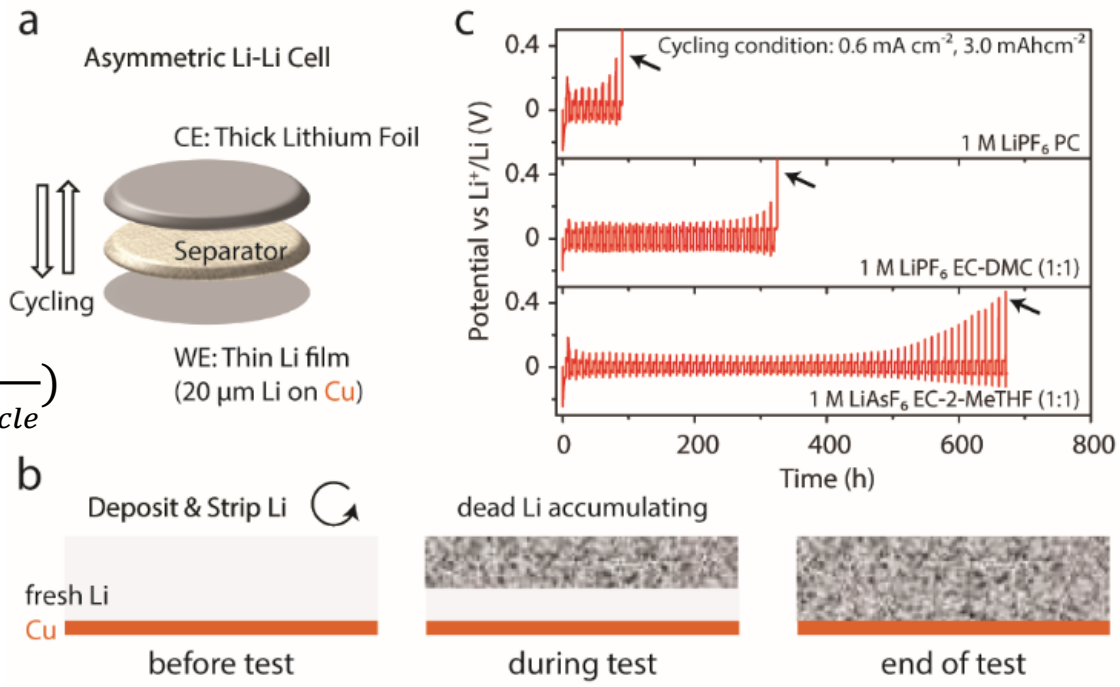
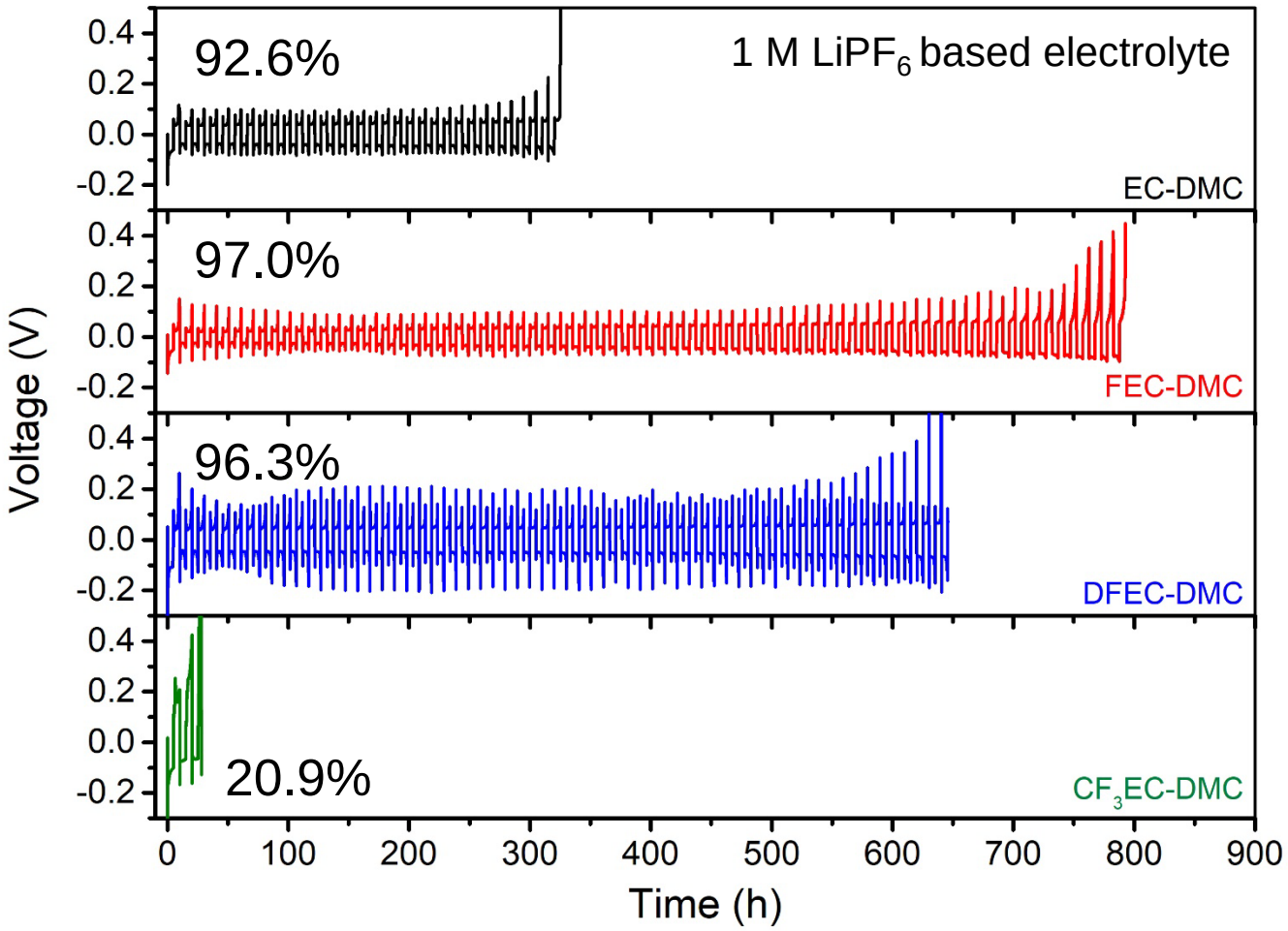
TECHNICAL ACCOMPLISHMENTS
DEVELOPMENT OF Li-Li ASYMMETRIC CELL TEST

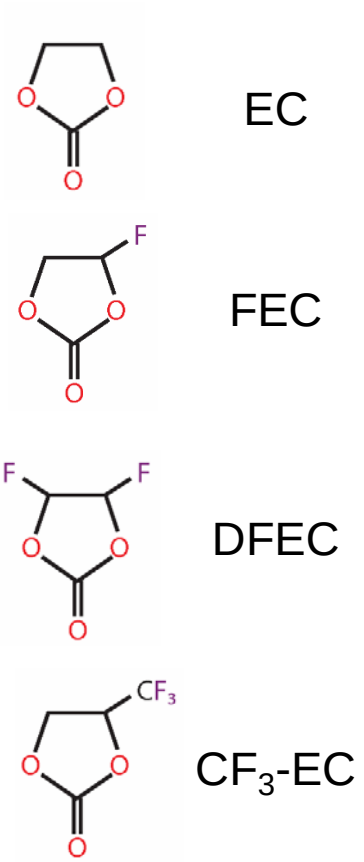
$$CE_{avg} = 1 - \left(\frac{Q_{total\ Li}}{n}\right) \cdot \left(\frac{1}{Q_{Li\ passed\ per\ cycle}}\right)$$
$$= 1 - \frac{Q_{Li\ passed\ per\ cycle} + Q_{Li}}{nQ_{Li\ passed\ per\ cycle}}$$



- Developed a reliable approach to measure CE and compare effect of Li salts, solvents, and additives
- Final voltage spike can be used to confirm the absence of short-circuit during the cycling test. (meeting Q8 milestone: Establish quantitative criteria for effectiveness and reproducibility in dendrite-suppression experiments)

TECHNICAL ACCOMPLISHMENTS
COMPARISON OF DIFFERENT FLUORINATED SOLVENTS

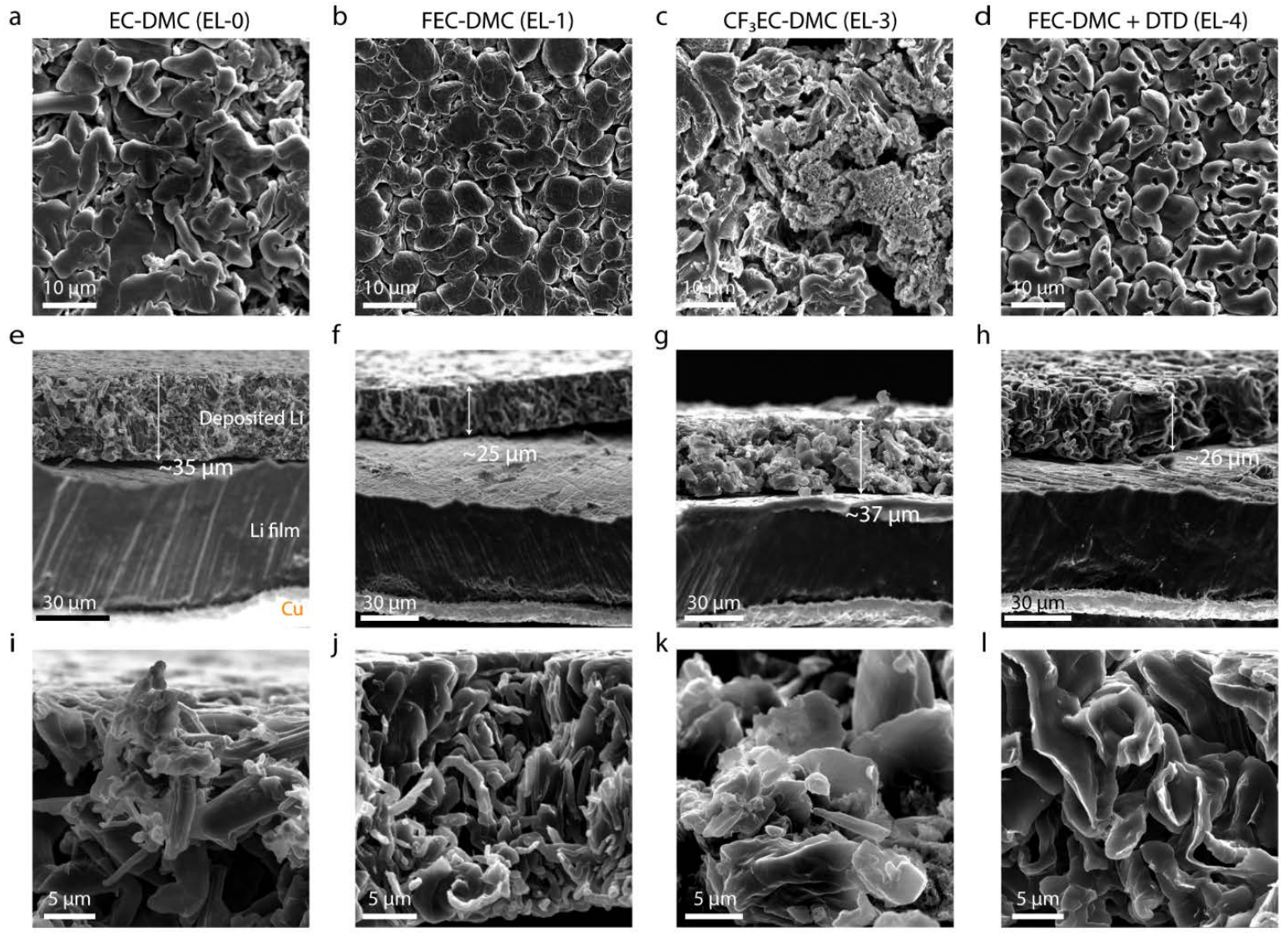




- Li-Li asymmetric cell test, area capacity: 3.0 mAh/cm^2, current Density: 0.6 mA/cm^2
- Average CE: FEC > DFEC > EC >> CF_3-EC, why?

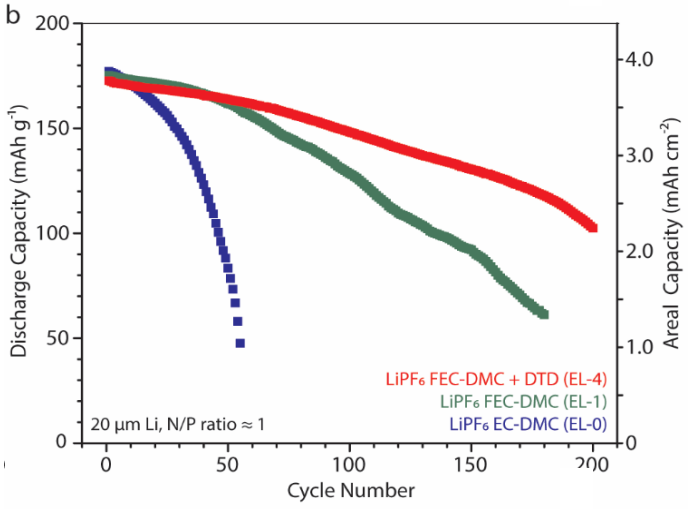
TECHNICAL ACCOMPLISHMENTS

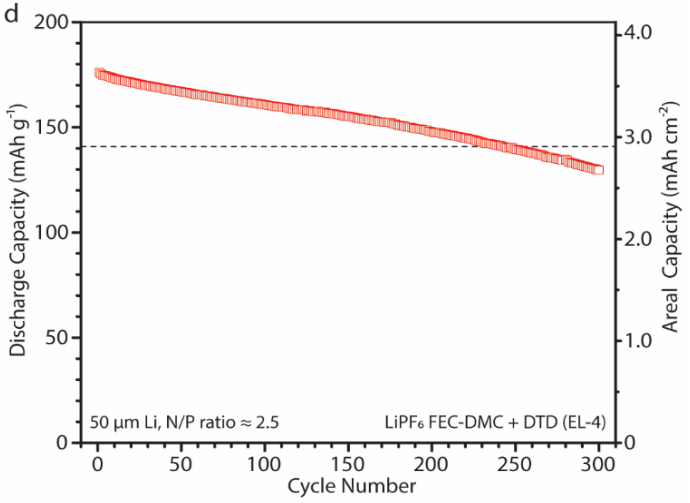
Direct observations of Li metal surface using SEM

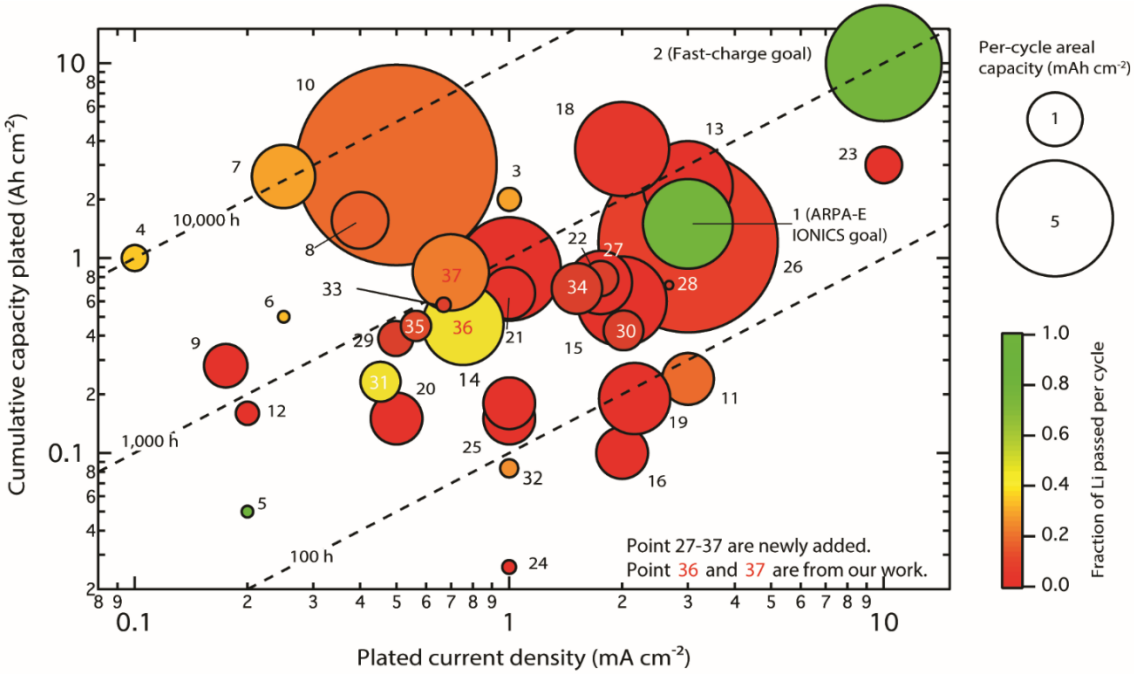


- LiF-rich SEIs promote dense Li deposition.

TECHNICAL ACCOMPLISHMENTS
FULL CELL CYCLING







Y. Zhu, V. Pande, L. Li,S. Pan, B. Wen, D. Wang, V. Viswanathan, Y.-M. Chiang, under review, arXiv:1903.09593.

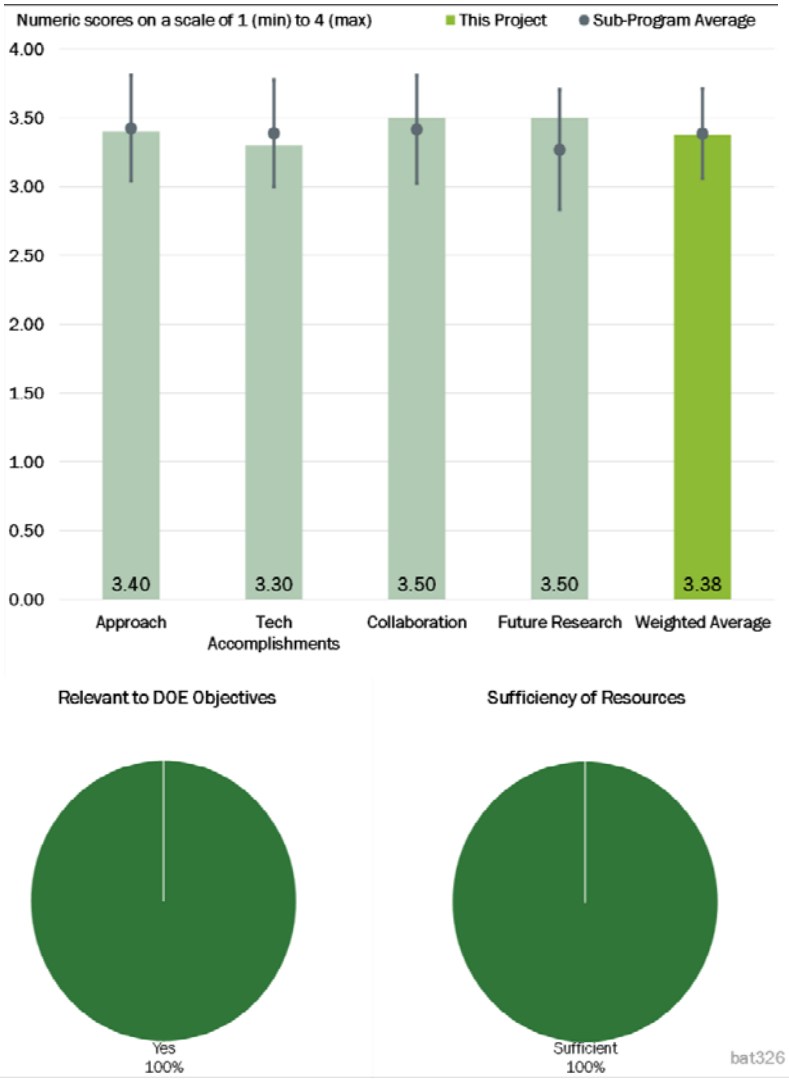
Responses to Previous Year Reviewers' Comments

Comment: The reviewer was not sure of the value of DFT to predict the effect of adding fluorinated solvent on the surface.

Response: We have identified quantitative descriptors based on DFT calculations that clearly show effectiveness of fluorinated solvents for forming high-performing SEIs.

Comment: The reviewer commented that the team left Q_{excess} undefined and the reviewer found that it is difficult to understand the physical significance.

Response: This has been clearly explained in our recent paper [arXiv:1903.09593].



Responses to Previous Year Reviewers' Comments

Comment: The reviewer commented that 70 cycles in a full cell is not particularly good. The Battery 500 Consortium recently showed over 200 cycles with a lean electrolyte and thin Li metal.

Response: Our team has now demonstrated comparable performance, > 250 cycles with thin lithium.

Comment: The reviewer advised that the team needs to strengthen collaborations to accomplish this project with more efficiency.

Response: The team has further strengthened collaborations and transferred liquid electrolytes from this project to 24M, which has been used to build larger format cells that perform better than baseline.

Comment: The reviewer said if the poor full cell cycling is due to low CE, then that is what needs attention.

Response: The team has focused on improving CE (~98%) and as a result, demonstrated improvement in full cell cycling (~ 250 cycles).

Collaboration and Coordination with Other Institutions

- **24M Technologies Inc**.
  - Tested electrolytes developed in this project in coin cells; outperforms their baseline
  - Fabrication and testing of 18 cm^2/80 cm^2 pouch cells (ongoing and future work)
  - Delivered high-performing electrolytes for integration in their full cell format.

Remaining Challenges and Barriers

- Uncontrolled but important variable is stack pressure
- Demonstrate retention of self-healing ability over longer cycle and calendar times.
- Deliver >10 mAh capacity cells.

Proposed Future Research

- **New Solvents/Salts:** Other fluorinated solvents/salts identified through theory for self formation and self healing to be experimentally tested.
- **Stack pressure:** Examine the effect of pressure on coulombic efficiency and density of electrodeposited metal.

Summary

Relevance

- Self-formed lithium halide based solid electrolyte interface, with the goal of enabling and demonstrating self-assembling/self-healing batteries using lithium metal negative electrodes.
- Simple and scalable path towards lithium metal electrodes and batteries with very high energy density (>350 Wh/kg).

Approach

A tightly integrated experiment-theory approach towards enabling self-formed lithium electrodes.

- Theory Approach: Use density functional theory calculations to down-select self-forming and self-healing halogenated electrolyte additives.
- Experimental approach: Assemble and test asymmetric cells as a screening approach to determine overall columbic efficiency. Test downselected electrolytes in full cells.

Technical Accomplishments

- Integrated theory+experiment selection of halogenated electrolyte additives for improving Li metal stability and cycle life.
- New asymmetric Li-Li cell methodology quantifies Coulombic efficiency and differentiates dendritic/non-dendritic behavior of Li electrodes.
- Identified new electrolytes that outperform baseline electrolytes in Li-Li asymmetric and $LiCoO_2$-Li full cells

Proposed Future Work

- Theoretical identification and quantification of new classes of fluorinated solvents for self formation and self healing.
- Structural and chemical characterization of lithium metal surface with different fluorinated solvents.
- Demonstrate Li metal full cells cycling at ≥ 3 mAh/cm^2 over >250 cycles.